Complexation of Arsenite with Humic Acid in the Presence of Ferric Iron

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Abstract

In the presence of iron (Fe), dissolved organic matter (DOM) may bind considerable amounts of arsenic (As), through formation of Fe-bridged As-Fe-DOM complexes and surface complexation of As on DOM-stabilized Fe-colloids (collectively referred to as As-Fe-DOM complexation). However, direct (e.g., chromatographic and spectroscopic) evidence and fundamental kinetic and stability constants have been rarely reported for this As-Fe-DOM complexation. Using a size exclusion chromatography (SEC)-UV-inductively coupled plasma mass spectrometry (ICP-MS) technique, arsenite (As[III])-Fe-DOM complexation was investigated after adding As[III] into the priorly prepared Fe-DOM. A series of evidence, including coelution of As, Fe, and DOM from the SEC column and coretention of As, Fe, and DOM by 3 kDa MWCO centrifugal filtration membrane, demonstrated the occurrence of As[III]-Fe-DOM complexation. The kinetic data of As[III]-Fe-DOM complexation were well described by a pseudo-first order rate equation ($R^2 = 0.95$), with the rate constant (k') being 0.17±0.04 1/h. Stability of As[III]-Fe-DOM complexation was characterized by apparent stability constant (K_s) derived from two-site ligand binding model, with log K_s ranging from 4.4±0.2 to 5.6±0.4. Considering the kinetics (within hours) and stability (similar to typical metal-humates) of As[III]-Fe-DOM complexation, this complexation needs to be included when evaluating As mobility in Fe and DOM rich environments.

Introduction

Dissolved organic matter (DOM) critically affects the environmental behavior and fate of arsenic (As) (1–3), a toxic element that poses a human health risk to millions of people worldwide (4–7). DOM can compete with As for adsorption sites at mineral surfaces and/or bind As species forming dissolved/colloidal As-DOM complexes, both of which may increase the mobility of As and have been related to the enhanced release of As from aquifer materials, soils, and sediments into groundwater (1,2,8–14). The formation of As-DOM complexes has been documented to various degrees depending on As species (e.g., arsenate, As[V], or arsenite, As[III]) and DOM type, among other factors (1,15–24). It has been observed that in some cases As-DOM complexation can have a significant effect on As mobilization and has to be considered in the investigation of As mobility (15,18,20–22,25).

The formation of As-DOM complexes could be a result of direct association of As with DOM, since DOM contains multiple functional groups such as sulfhydryl and amine which could bind As through ligand exchange (1,21,22,24). However, recent studies have suggested that metals (in particular Fe) may play an important role in As-DOM interaction

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(15,22,25,26). Ritter et al. (15) observed a linear relationship between the amount of complexed As^V and the Fe content of the DOM when investigating As complexation with DOM samples amended with Fe. Similarly, Bauer and Blodau (25) found a strong correlation between As and Fe present in dissolved, colloidal, and particulate fractions in DOM and Fe rich solutions. Sharma et al. (22) observed almost no As complexation by Fe-free DOM, but considerable amounts (~3.5–8 μg As/mg DOC) of As^V associated with Fe-DOM. All these results demonstrate the essential role of Fe in increasing As binding capacity of DOM, possibly through the formation of Fe-bridged dissolved/colloidal As-Fe-DOM complexes and association of As with DOM-stabilized Fe-colloids (collectively referred to as As-Fe-DOM complexation throughout the paper, unless stated otherwise).

Despite the importance of Fe-involved As-DOM complexation, direct (e.g., chromatographic and spectroscopic) evidence for As-Fe-DOM complexation is rare. Sharma et al. (22) provided spectroscopic evidence using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy to support As^V-Fe-DOM presence in As amended Fe-DOM samples, by observing a frequency shift in carboxyl stretching bands (compared to Fe-DOM samples without As). However, the products of As-Fe-DOM complexation have never been separated from unbound As by using a chromatography-based analytical technique. In addition, fundamental parameters (including kinetic and stability constants) for characterizing As-Fe-DOM complexation remain lacking, which hampers further evaluating the role of As-Fe-DOM complexation in regulating As mobility and bioavailability.

The objectives of this study were 1) to provide direct evidence for As^{III}-Fe-DOM complexation by chromatographically separating the products formed through this process from free As^{III} in one analytical run, and 2) to characterize As^{III}-Fe-DOM complexation by calculating kinetic rate and apparent stability constants (K_s) of resulting products. In this study, As^{III} was added to Fe-DOM complexes/colloids (priorly prepared by adding Fe to humic acid) to form As^{III}-Fe-DOM complexation. Free and Fe-DOM complexed As^{III} were then directly determined by using a size exclusion chromatography (SEC)-UV-inductively coupled plasma mass spectrometry (ICP-MS) analytical technique.

Methods and Materials

Materials

As^{III} standard solutions were prepared by dissolving desired amounts of sodium meta-arsenite (98%, Aldrich) in deionized water (DIW, 18 MΩ-cm). Fe^{III} stock solutions were made with reagent grade $FeCl_3 \cdot 6H_2O$ (Fisher Scientific). Humic acid (HA, sodium salt) was purchased from Sigma-Aldrich. All other chemicals used were of analytical or trace metal grade.

Analyses

Speciation of free and Fe-DOM complexed As^{III} was performed using a SEC-UV-ICP-MS method reported in our previous study (24). Anion exchange HPLC coupled to hydride generation atomic fluorescence spectrometer (AE-HPLC-HG-AFS) was used as an ancillary method for As speciation. Dissolved organic matter concentration (DOC) was measured using a Shimadzu TOC 5000 analyzer. Total As and Fe were measured employing an atomic absorption spectrometer (AAS).

Preparation of Fe-DOM Solution

A Fe-DOM stock solution was prepared by adding Fe^{III} into HA solution at pH 8–9, according to a previously reported procedure (27). In this solution, Fe was predominantly

(>95%) present in DOM-complexed/colloidal form, whereas free Fe is nominal (see Results and Discussion below).

As^{III}-Fe-DOM Complexation Experiments

For As^{III}-Fe-DOM complexation experiments, a diluted Fe-DOM solution was prepared by diluting the Fe-DOM stock solution 600 times with DIW (the concentrations of DOC and Fe in the diluted solution were 14 and 2.4 mg/L, respectively) and adjusting the pH to 7.8. By adding As^{III} standard to the diluted Fe-DOM solution to achieve desired concentrations, the following experiments were conducted: 1) Detection of As^{III}-Fe-DOM complexation; 2) Kinetics of As^{III} complexation with Fe-DOM; and 3) Stability of As^{III}-Fe-DOM complexation. These experiments were carried out by putting the As^{III}-Fe-DOM mixtures on a shaker, taking samples at appropriate intervals, and analyzing the samples on SEC-UV-ICP-MS for free and Fe-DOM complexed As after centrifugation and filtration.

For Experiment 1, several tests were further conducted to crosscheck As^{III}-Fe-DOM complexation. These tests include: 1) The As^{III}-Fe-DOM solutions were analyzed by AE-HPLC-HG-AFS for presence of common environmental As species which include As^{III}, As^{V}, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA); 2) The As^{III}-Fe-DOM solutions were spiked with As^{V}, MMA, or DMA and then immediately analyzed using SEC-UV-ICP-MS to check the interference of other As species on detection of Fe-DOM complexed As^{III}; 3) The As^{III}-Fe-DOM solutions were acidified by adding concentrated HCl or HNO$_3$ (the final concentrations of acid were about 10%, v/v) and then analyzed for As species employing SEC-UV-ICP-MS and AE-HPLC-HG-AFS; and 4) Centrifugal filtration devices with 3 kDa and 1 kDa molecular weight cut-off (MWCO) were used to separate free and bound As in the As^{III}-Fe-DOM mixture (see Supporting Information).

Additional experimental information, including instrumental set-up, preparation of HA and Fe-DOM solutions, and complexation experiments can be found in Supporting Information. All experiments were conducted in duplicate and the average was reported unless otherwise stated. During the course of the experiments, conversion of As^{III} to As^{V} was not observed, as evidenced by the absence of As^{V} peak in speciation analysis. The adsorption loss of As^{III} by bottle/vial walls or filters was negligible, with As^{III} mass balances being 100±10 % for all experiments.

Data Analysis

Kinetics of complexation of As^{III} with Fe-DOM was characterized by a pseudo-first order rate constant, k', as in Equation 1

$$\frac{dC_b^{As}}{dt} = k_1 C_{Fe-DOM} C_f^{As} = k' C_f^{As}$$

(1)

where C_f^{As} and C_b^{As} are free and Fe-DOM bound As^{III} concentrations in M, respectively. C_{Fe-DOM} is the molar concentration of effective ligands contained in Fe-DOM in M. k_1 is the complexation rate constant in L/mol/h while k' is the pseudo-first order complexation rate constant in 1/h. Nonlinear regression was performed by applying the integral form of Equation 1 to fit the experimental data to obtain k'.

The stability of As^{III}-Fe-DOM complexation was estimated using an apparent stability constant (K_s, L/mol)

$$K_s = \frac{C_b^{As}}{C_f^{As} \times C_{Fe-DOM}}$$

(2)

K_s was determined by employing a previously used method (24), which includes the Scatchard plot (27–29) and ligand binding model (see Supporting Information).

Results and Discussion

Formation of Fe-DOM Complexes/Colloids

The SEC-UV-ICP-MS analysis of Fe-DOM solution prepared under the current experimental conditions shows the coelution of Fe and DOM (Fig. S1b). The Fe peak coeluted with DOM was not caused by free Fe (not associated with DOM) because injection of FeCl$_3$ solution (containing ~2 mg/L of Fe) did not generate Fe peaks on SEC-UV-ICP-MS (Fig. S1c). The Fe in Fe-DOM solution was not from the Aldrich HA background, as evidenced by the absence of Fe peak on the chromatogram of the bare HA (Fig. S1a). These results indicate that the Fe^{III} added during preparation of Fe-DOM was indeed associated with HA.

Total Fe and DOC analysis of As^{III}-Fe-DOM solution after centrifugal filtration (3 kDa MWCO) suggests that most Fe and DOM in Fe-DOM can be retained by filtration and thus in the colloidal form (> 3 kDa) (see below for results of As^{III}-Fe-DOM complexation). This result agrees with our laboratory observation that typically > 95% of the HA (with or without Fe addition) would be removed through these types of centrifugal filtration devices. The colloidal Fe-DOM prepared here could be present in (at least) two different forms. First, upon addition of Fe to HA solutions, Fe acted as bridges to interconnect DOM molecules, which could induce coagulation of DOM to form Fe-DOM complexes (Fe-rich colloidal DOM) (15,22). Second, after adding Fe to HA solutions, a stable suspension of Fe-colloids, e.g., as (oxy)hydroxides, was formed due to the stabilizing effect of DOM. The formation of stable Fe-colloids (probably coated by OM due to adsorption of OM) in the presence of DOM has been demonstrated by a number of studies (15,22,30). For example, Ritter et al. (15) suggested that a significant fraction (23–84%) of Fe in solution after filtration at 0.45 μm was present as colloids thanks to the stabilizing effect of DOM, whereas most of Fe was precipitated and then removed from solution through 0.45 μm filtration in the absence of DOM.

The colloidal Fe-DOM complexes and the DOM-stabilized Fe-colloids formed through these two processes cannot be differentiated and thus were collectively referred to as Fe-DOM complexes/colloids here. The Fe complexation capacities for DOM are reported in the range from 0.1 to 30 mmol Fe/mol C (31) or even lower (32). There are 14 mg/L DOC and 2.4 mg/L Fe in the solution prepared here, indicating a much higher Fe/DOC ratio than the reported Fe complexation capacities. Thus the DOM-stabilized Fe-colloids could be the major fraction of Fe-DOM complexes/colloids. The Fe-colloids formed in the presence of DOM can be much smaller than without DOM. This could be one of possible reasons why no Fe peak was detected when only FeCl$_3$ was injected to SEC-ICP-MS, where no Fe eluted off the column due to formation of big Fe-colloidal particles. In the case of Fe-DOM solution, Fe was either complexed by DOM to form Fe-DOM complexes or stabilized by DOM to form small Fe-colloids, where Fe could elute out of the column along with DOM and be detected. It should be mentioned that the experimental HA solutions used here did contain ~0.07 mg/L of inherent Fe (determined for total Fe by AAS), but no Fe could be detected when using SEC-UV-ICP-MS. This could be due to the low concentration of inherent Fe (the detection limit of Fe on SEC-ICP-MS is about 0.2 mg/L, estimated as 3

times background noise) or because the Fe in HA solutions was not present in the DOM-complexed form.

Detection of Fe-DOM Complexed As[III]

The SEC-UV-ICP-MS analysis of As[III]-Fe-DOM solutions reveals the coelution of As, Fe, and DOM (Fig. 1a). The As coeluted with DOM was not from the background of HA or Fe-DOM used here, because the analysis of HA and Fe-DOM controls (without addition of As) suggests that no detectable As was originally present in the HA purchased or in the Fe-DOM prepared (Fig. S1). The As coeluted with DOM was clearly an As species different from free As[III], based on the different retention times of these two species, suggesting possible As[III]-Fe-DOM complexation after mixing As[III] with Fe-DOM. At initial As[III] concentration of 50 μg/L, the Fe-DOM prepared in this study bound significantly more As (about 20–25% of As after 48 h contact), in comparison to the bare HA (Fig. 1b, where less than 5% of As was complexed). For As[III]-Fe control experiments, only free As[III] appeared on the chromatogram, indicating no As[III] being complexed by Fe in the absence of DOM (Fig. S1c). These results suggest that the presence of Fe in HA significantly promoted the association of As[III] with DOM. Multiple lines of evidence further support the occurrence of As[III]-Fe-DOM complexation in the mixture of As[III] with Fe-DOM.

First, the possible interference of other As species with As[III]-Fe-DOM detection was eliminated through As speciation using different techniques and spike experiments. For the SEC-UV-ICP-MS method used in this study, Fe-DOM complexed As[III] eluted from the SB-802.5 HQ column at about 220 s, whereas the retention time for free As[V], MMA, and DMA was 290 s. The SEC-UV-ICP-MS analyses of As[III]-Fe-DOM solutions suggest the absence of As[V], MMA, and DMA in the experimental solutions. The results of AE-HPLC-HG-AFS analyses revealed that, among all common As species (As[III], As[V], MMA, and DMA) this technique is capable of detecting, As[III] was the only As species detected (Fig. S2c), which confirms the absence of As[V], MMA, and DMA in the experimental solutions. It should be noted that due to the fact that the anion exchange column can retain DOM-bound As, AE-HPLC-HG-AFS failed to reveal the presence of Fe-DOM complexed As[III]. In order to further eliminate the possibility of misidentification of other As species (As[V], MMA, and DMA) as Fe-DOM complexed As[III], these As species were individually spiked into the experimental solutions. The analysis of spiked solutions indicates that the presence of these three As species did not interfere with As[III]-Fe-DOM detection. Fig. S2 shows the results for As[V]-spiked solutions, whereas similar results were observed for MMA and DMA spiking and not shown.

Second, the analytical results of the As[III]-Fe-DOM solutions after acidification confirmed that the As species complexed by Fe-DOM is As[III], as evidenced by the appearance of only free As[III] after acidification using HCl or HNO_3 (Figs. S2 b and d). Both SEC-UV-ICP-MS and AE-HPLC-HG-AFS gave only one As[III] peak for the acidified samples (Fig. S2 shows the results of HNO_3 acidification only). It is unlikely that the As bound by Fe-DOM was As[V] and reduced to As[III] during acidification, in particular in the case of HNO_3 which is an oxidative acid.

Third, after centrifugal filtration through 3 kDa or 1 kDa MWCO membranes, no DOM peak was observed with UV detection at 254 nm for the filtrates (Fig. S3b). This suggests that most DOM was in the colloidal form (> 3 kDa) and retained by filtration, which was confirmed by measuring DOC concentrations in the filtrates and retentates (Fig. 2). The chromatograms for 3 and 1 kDa MWCO filtration were identical and Fig. S3 illustrated the typical chromatograms for 3 kDa MWCO filtration. Also in the filtrates, neither Fe nor As was detected at the retention time of DOM (Fig. S3b), indicating that the coelution of DOM, Fe, and As in the original solution (Fig. 1a) did correspond to As[III]-Fe-DOM complexation.

In fact, only free As^{III} can be detected in the filtrates (Fig. S3b). In contrast to the filtrates, the coelution of DOM, Fe, and As was observed in the retentates (in addition to free As^{III}) (Fig. S3a), indicating the retention of colloidal products of As^{III}-Fe-DOM complexation by the filtration membrane, as is the case of HA. These results conform to the presumption that the As peak coeluted with DOM and Fe is in the Fe-DOM complexed form.

The concentrations of As, Fe, and DOC in the filtrates and retentates provided further evidence for the presence of As^{III}-Fe-DOM complexation. As expected, most of DOM and Fe were present in the retentates, with Fe concentrations in the retentates being 2–3 orders of magnitude higher than in the filtrates (Fig. 2). Note that the volume ratio of retentate to filtrate was different for 1 kDa filtration (~1.3/1.7) than for 3 kDa (~1.8/1.2) when 3 ml of original solution was taken for separation, which was the reason for the concentration differences between 1 and 3 kDa filtration. Calculations taking the volume differences into account suggest that 2.2–2.4 mg/L of Fe was complexed by HA whereas the free Fe was only about 0.07–0.08 mg/L in the As^{III}-Fe-DOM solutions, with the results for 1 and 3 kDa filtrations being consistent. The calculations also show that the concentrations of free As^{III} and Fe-DOM bound As^{III} were ~35 and 11–13 μg/L (initial As^{III} = 50 μg/L), respectively, agreeing well with SEC-UV-ICP-MS analysis and producing a satisfying mass balance of As (92–96%). It should be noted that the Fe concentrations in the filtrates are much higher than the solubility of amorphous/nanocrystalline Fe oxyhydroxide (ferrihydrite), which is about 10^{-9} M in the 7–9 pH range (33). Such high dissolved Fe concentrations could be related to the complexation of Fe with small organic ligands (although low, there is still 3–4% of DOM in the filtrates) and/or small Fe-oxyhydroxide colloids passing through the filtration membranes.

Kinetics of As^{III}-Fe-DOM Complexation

The concentrations of As^{III} bound by Fe-DOM increased rapidly at the beginning of the kinetic experiment and reached a plateau approximately after 20 h (Fig. 3a). For example, immediately after adding As^{III} to Fe-DOM (initial As^{III} = 100 μg/L or 1.3 μM), an aliquot of the mixture was sampled, filtered, and analyzed and the concentration of Fe-DOM bound As^{III} was 0.024 μM. Fe-DOM bound As^{III} was 0.14 μM after 12 h and further increased to 0.17 μM after 30 h. Our results are in general agreement with those of Warwick et al. (18), who used an equilibration time of 24 h for studying complexation of HA with As^{III} and As^V. Bauer and Blodau also found that association between As^V, Fe, and DOM could reach equilibrium after 24 h in larger colloid fraction (50 kDa-0.2μm), although longer reaction time (up to 144 h) was needed for smaller colloid fraction (5–50 kDa) (25). However, in previous dialysis studies on complexation of As with DOM (with or without addition of metals) (15,21,22), longer times (e.g., up to 2 weeks) were sometimes needed for complexation of As species (in particular As^V) with DOM to reach equilibrium. This is likely related to the diffusion of As through dialysis membrane.

The kinetic data of As^{III} complexation with Fe-DOM in the current study were well described by a pseudo-first order rate equation (coefficient of determination R^2 = 0.95, P<0.0001) (Fig. 3a). The pseudo-first order rate constant, k', was determined to be 0.17±0.04 1/h, which corresponds a $t_{1/2}$ of about 4 h. The kinetic constants of As^{III} complexation with Fe-DOM have not been reported previously, which limits the comparison between our results and the literature.

The prepared Fe-DOM could be present in two forms: Fe-bridge interconnected Fe-DOM complexes and DOM-stabilized Fe-colloids (15,22). Accordingly, As^{III}-Fe-DOM complexation may occur via two processes: chelation of As^{III} by Fe bridges entrained within Fe-DOM complexes and surface complexation of As^{III} to the surface sites of DOM-stabilized Fe-colloids, as proposed by Ritter et al. (15) and Sharma et al. (22). Both

processes were possible in the current study, and surface complexation of As^{III} to the DOM-stabilized Fe-colloids might be the major one since a high Fe/DOC ratio was used here (see the results of Fe-DOM preparation above). The equilibration time of As^{III}-Fe-DOM complexation in this study (> 20 h) is longer than for As^{III}-Fe (oxy)hydroxides surface complexation (which is usually within 2–4 h) (34–36). This could be due to the coexistence of Fe-bridged As^{III} chelation and As^{III} surface complexation to Fe-colloids, or the adsorption of DOM on Fe-colloids (which would compete with As for adsorption sites and result in a slower As adsorption process).

Apparent Stability Constants of As^{III}-Fe-DOM Complexation

The Scatchard plot (C_b^{As}/C_f^{As} versus C_b^{As} at different initial As concentrations) showed that the data points appeared to deviate from linearity (dots in Fig. S4). The K_s for the As^{III}-Fe-DOM complexation could not be determined directly from the slope of the Scatchard plot, since there appeared to be at least two distinct slopes for the plot. The experimental data were then fitted into the ligand binding model to determine K_s and B_{max} (maximum binding capability of Fe-DOM toward As^{III} in M under the experimental conditions). The fitting of two-site ligand binding model corresponded to a coefficients of determination (R^2) of 0.97 (with P < 0.0001, Fig. 3b). Therefore we used the results of two-site fitting to describe the complexation of As^{III} with Fe-DOM, by classifying the binding site in Fe-DOM into two groups. The first group (S1) consists of strong sites corresponding to complexation with higher stability occurred at low As^{III} concentrations, whereas the second group (S2) corresponded to weak sites where complexation with lower stability occurred at high As^{III}.

The log K_s for these two types of complexation were 5.6±0.4 for S1 sites and 4.4±0.2 for S2 sites (Table 1). Correspondingly, B_{max} was 0.40±0.16 μM for S1 sites and 0.74±0.44 μM for S2 sites. Although the K_s for S1 sites is an order of magnitude higher (statistically significant, *t*-test, P<0.001) than for S2 sites, the B_{max} for S1 sites is significantly lower (*t*-test, P<0.001), in comparison to S2 sites. Considering surface complexation of As^{III} with DOM-stabilized Fe-colloids could be the major form of As^{III}-Fe-DOM complexation, the differences between S1 and S2 sites in B_{max} were possibly related to the As species formed on Fe-colloidal surface. Stachowicz et al. have shown that two types of surface species of As^{III} can be formed on goethite surface: one bidentate (log K = 7.3) and one monodentate (log K = 4.9) (37). Because the high affinity bidentate species requires two surface sites, this may explain the smaller B_{max} for S1 sites where As^{III} concentrations are low and thus formation of bidentate species is favorable.

The concentrations of Fe bound by HA in the current study was 2.4 mg/L (~43 μM) in the experiments of determining K_s for As-Fe-DOM complexation. The total B_{max} (S1+S2 sites) was 1.1 μM, amounting only to about 2.6% of total Fe present in Fe-DOM. These data suggest a significant excess of Fe bridges or Fe-colloids surface binding sites compared to the amount of As complexed. These results agree well with a pervious study where the molar ratios of complexed As to Fe were 0.02–0.05 for As^V complexation with Fe-DOM, suggesting that 2–5% of Fe could be accountable for all As^V-Fe-DOM complexation (22). In contrast to these results, Ritter et al. (15) observed a consistent ratio of complexed As^V to Fe to be 0.2 through a wide range of Fe concentrations (5–210 μM). Previous studies also show that at environmentally relevant pH Fe (oxy)hydroxides have densities of surface sites in the range of 0.1–0.2 mol of sorption sites per mol of Fe for complexing cations, oxyanions (e.g., As^V), and neutral species (e.g., As^{III}) (34,35,38–42). The relative low As binding capacity of Fe present in Fe-DOM under the current experimental conditions (about 0.026 mol of As^{III} per mol of Fe) could be due to the adsorption of DOM (which would reduce the As binding capacity of Fe-colloids) and/or the experimental conditions (e.g., pH 7.8, at which As

adsorption is relatively weak and the maximum binding capacity of Fe-oxides cannot be reached).

The K_s of As-Fe-DOM complexation has not been reported previously, although two recent studies that were directly designed to investigate As-Fe-DOM complexation did report the free and Fe-DOM bound As concentrations (15,22). In order to obtain complementary information on the magnitude of K_s values of As-Fe-DOM complexation, we estimated K_s for these two studies directly according to Equation 2 by using data reported there. The $C_{Fe\text{-}DOM}$ in Equation 2 was estimated based on the concentration of complexed Fe, since direct As-DOM complexation (without Fe) was rather small (15,22). For the study of Ritter et al. (15), the log K_s was estimated to be 5.0–5.1 for As^V-Fe-DOM (Table 1), assuming 0.2 mol of As binding sites per mol of Fe as observed by the authors. For the study of Sharma et al. (22), the log K_s was estimated to be about 5.4 for As^V-Fe-DOM, assuming 0.05 mol of As binding sites per mol of Fe as reported by the authors. These estimated K_s values appear to be in between our K_s for S1 sites and for S2 sites. When one-site ligand binding model was used to fit our isotherm experimental data, a log K_s of 5.2±0.2 was produced, which represents an averaged K_s for all binding sites composited together. It seems that the K_s values of As-Fe-DOM complexation (estimated for all three studies, ours and the other two in the literature) are within the typical range of K_s for metal-humic complexes (log K_s around 4–6) (27). It is necessary to mention that the experimental methods and conditions, including As species (As^{III} or As^V), employed in these three studies differ to some extent (Table 1), despite that comparable K_s values were obtained for these studies.

Environmental Considerations

The current study demonstrated that 1) In the presence of Fe, DOM can bind considerable amounts of As^{III} through As^{III}-Fe-DOM complexation, and 2) This complexation occurs within a time span of hours and bears comparable orders of K_s with typical metal-humates. The magnitude of As^{III} bound by Fe-DOM and the kinetic and stability data suggest that As^{III}-Fe-DOM complexation could play an important role in regulating As mobility and bioavailability in the environments rich in DOM and Fe (and possibly Al (21)). For instance, our previous studies have shown substantially increased dissolution of Fe and Al from soils in the presence of DOM, probably due to the colloids released from soils induced by DOM which could stabilize the Fe- and Al- colloids (23,43). The DOM-stabilized Fe-colloids in soil solutions could further bind As and subsequently affect As transport to percolate water through leaching and to surface water through runoff. In addition, aquatic DOM itself may contain a considerable amount of inherent Fe (e.g., up to ~40 mg/L has been observed for DOM from natural waters) (15,22,24,25), in which case there would be increased potential for As to be complexed by DOM through the role of high levels of Fe. However, it should be pointed out that a commercial (Aldrich) HA, which is extracted from lignite (a form of coal), was used in this study. Concerns surrounding the use of commercial HAs in water and soil research have been raised in previous studies, due to pronounced differences in chemical properties between commercial (including Aldrich) and natural HAs (44). Cautions need to be exercised when extending the current research results to the realistic environments and more studies using DOM from natural soil or water sources are warranted.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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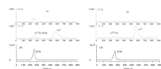
Fig. 1.
SEC-UV-ICP-MS chromatograms of As^{III} (50 µg/L) complexation with (a) Fe-DOM (Fe=2.4 mg/L and DOC=14 mg/L) and (b) bare Aldrich HA (DOC=14 mg/L). Detection of Fe and As on ICP-MS and DOM peak on UV are shown in the chromatograms.
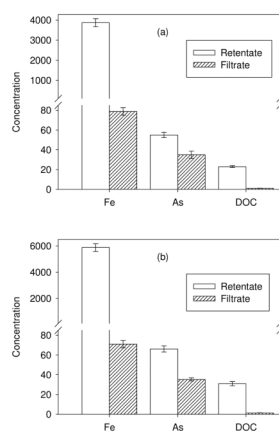
Fig. 2.
Distribution of Fe, As, and DOC present in As^{III}-Fe-DOM solutions (initial As^{III}=50 µg/L, Fe=2.4 mg/L, and DOC=14 mg/L) between the retentates and filtrates after centrifugal filtration through (a) 1 kDa and (b) 3 kDa MWCO devices. Concentrations of Fe and As are in µg/L while DOC in mg/L.
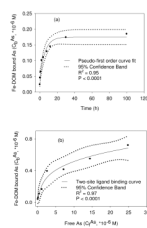
Fig. 3.
(a) Kinetic data of As^{III} (initial As = 100 µg/L) complexation with Fe-DOM (Fe=2.4 mg/L and DOC=14 mg/L). (b) Calculation of K_s and B_{max} of As^{III}-Fe-DOM complexation through nonlinear regression using two-site ligand binding model.

Table 1

Apparent stability constants (K_s, L/mol) and maximum binding capabilities (B_{max}) of As^{III} complexation with Fe-DOM (±standard error) for this study. For the purpose of comparison, K_s and B_{max} of As complexation with DOM reported in the literature were illustrated. S1 and S2 represent loosely classified strong and weak binding sites, respectively, whereas total means all sites are classified into one group. AHA: Aldrich humic acid; SR-WW: Suwannee River whole water; EG-FA: Everglades fulvic acid fraction; PHA: Pahokee peat humic acid.

References	Binding site	Log K_s	B_{max} (μM)	Binding type	DOM Source	As (mg/L)	Fe (mg/L)	DOC (mg/L)	pH
This study	S1	5.6±0.4	0.40±0.16	As^{III}-Fe-DOM	AHA	0.01–2	2.4	14	7.8
	S2	4.4±0.2	0.74±0.44						
	Total	5.2±0.2	1.14±0.47						
Ritter et al. (15)	Total	5.0–5.1^a	-	As^V-Fe-DOM	SR-WW; EG-FA	0.72	2.3–2.5	20	6
Sharma et al. (22)	Total	5.4^a	-	As^V-Fe-DOM	PHA	0.16^b	3.3	30–50	7
Warwick et al. (18)	Total	0.5–2.5	-	As^{III}-DOM	AHA	0–100	Not added	1500^c	3–12
Liu et al. (24)	S1	6.5	0.011	As^{III}-DOM	AHA	0.005–1	Not added	14	7
	S2	4.8	0.31						

^{a}: estimated from the concentration data reported in the references;

^{b}: As^V concentration outside the dialysis bag after dialyzing the preformed As^V-Fe-DOM complex for 24 h;

^{c}: concentration of AHA.